Differences between L_3 and L_2 x-ray absorption spectra of transition metal compounds

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The differences between L_3 and L_2 edges of $3d$ and $4d$ transition metal complexes and compounds in octahedral symmetry are discussed. The main origin of these differences are the multiplet effects due to the coupling of the $2p$ core wave function and the $3d$ and $4d$ valence wave functions. The $3d$ and $4d$ spin–orbit coupling is a second origin of difference. For $3d$ systems the multiplet effects dominate all other interactions and the L_3 and L_2 edge are completely mixed and reordered. For $4d$ systems the core hole spin–orbit coupling is large and the L_3 and L_2 are separated by about 100 eV with a ratio close to 2:1. The differences between the L_3 and L_2 edge originate from the weight transfer between the t_{2g} and e_g peaks due to the multiplet effect. This weight transfer is about 25% for the L_3 edge and about 5% for the L_2 edge, which implies that for a comparison to single-particle calculations the L_2 edge is preferable to use. Partly filled $4d$ systems are low-spin and the occupation of the t_{2g} states implies a decrease of the first peak. This decrease is stronger for the L_2 edge, implying an increase in the L_3:L_2 ratio. For $4d^5$ systems transitions to the t_{2g} hole are only possible at the L_3 edge due to the combined effects of $4d$ spin–orbit coupling and the dd multiplet effects.

I. INTRODUCTION

This paper discusses the origins of the differences between the L_3 and L_2 edges. Within the single-particle model of x-ray absorption spectroscopy the L_3 and L_2 edges should be equivalent. Both edges are described as transitions from a $2p$ core state to the empty states of both s and d character. The distribution of empty states is then approximated with band structure calculations or alternatively with real space multiple scattering calculations.[1,2] The intensity of the L_3 edge ($j_{\text{core}}=3/2$) is two times that of the L_2 edge ($j_{\text{core}}=1/2$). They are separated by 3/2 times the core spin–orbit coupling (ζ_{2p}). Within a single-particle scheme the only possibility of differences between the spectral shape of the L_3 and L_2 edge is the spin–orbit coupling of the valence electrons.

The L_3 and L_2 edges of $3d$ and $4d$ systems are of quite different nature. For $3d$ systems the L_3 and L_2 edges are separated by an energy of only 5 to 20 eV. The L_3 edge is completely different from the L_2 edge for $3d$ transition metal compounds.[3,4] Also their branching ratio is far from 2:1 which is also the case for the pure $3d$ metals.[5] The origin for these large differences has been determined as a combination of (a) $3d$ spin–orbit coupling, (b) correlations within the $3d$ band, and (c) correlations between the $2p$ core hole and the $3d$ holes. The correlation effects can be restated in the terminology of atomic physics as "multiplet effects".[6] By adding the group theoretical conditions of the crystallographic point groups to the atomic multiplet programs[7,8] one can reproduce the L_3 and L_2 edges of $3d$ transition metal compounds to an excellent degree.[3,4] The multiplet effects completely modify the L_3 and L_2 edges from their single-particle interpretation. The multiplet effects of the $2p$ with the $3d$ states are of the order of 10 eV, that is of the same order of magnitude as the $2p$ spin–orbit coupling. The consequence is that they completely rearrange the spectral shapes compared to a single-particle picture. This includes a strong mixing of the $j_{\text{core}}=\frac{3}{2}$ and $j_{\text{core}}=\frac{1}{2}$ character, hence an intensity ratio which deviates from 2:1.[9]

For $4d$ systems the separation between the L_3 and L_2 edges is of the order of 100 eV. Furthermore, the coupling of the $2p$ core wave function with the $4d$ valence states is less strong, resulting in multiplet effects of the order of 2 eV only. The consequence is that the L_3 to L_2 ratio is always close to 2:1. Experiments have detected differences in the spectral shape for a series of $4d$ systems, e.g., compounds of zirconium,[10] molybdenum,[11,12] niobium,[13] and ruthenium.[14] One observes that the L_3 and L_2 edges are different and that the first peak of the crystal field split doublet is more intense in the L_2 edge compared with the L_3 edge. Often one has assumed that the $4d$ spin–orbit coupling is the sole origin of this difference, but we will show that the main reason for the difference between the L_3 and L_2 edges of the $4d$ systems are in fact the multiplet effects coupling the $2p$ core wave function to the valence states of $4d$ character.

In Sec. II we focus on the $3d$ systems with an empty band introducing step-by-step the interactions present: $2p$ spin–orbit coupling, crystal field effects, $3d$ spin–orbit coupling, and the $2p3d$ multiplet effects. In Sec. III we repeat this analysis for the $4d$ systems. Section IV discusses the consequences of a partly filled $4d$ band and in Sec. V we compare our results with experiment.

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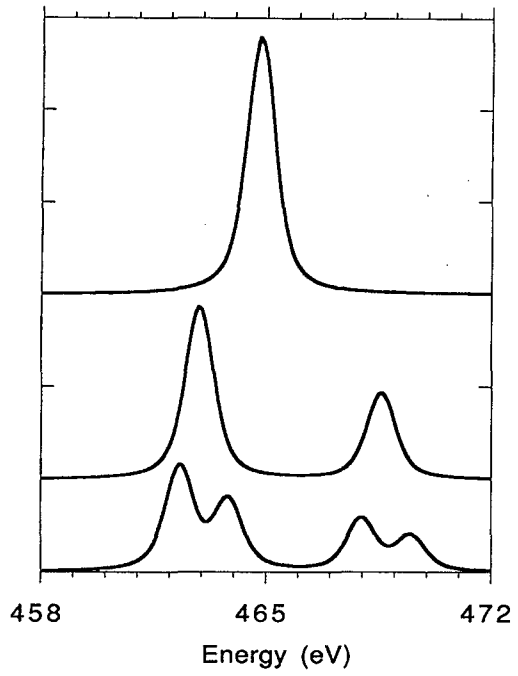

FIG. 1. Single-particle-like calculations for the transition $3d^0 \rightarrow 2p^5 3d^1$. Top: only energy difference; middle: inclusion of $2p$ spin–orbit; bottom: inclusion of crystal field splitting.

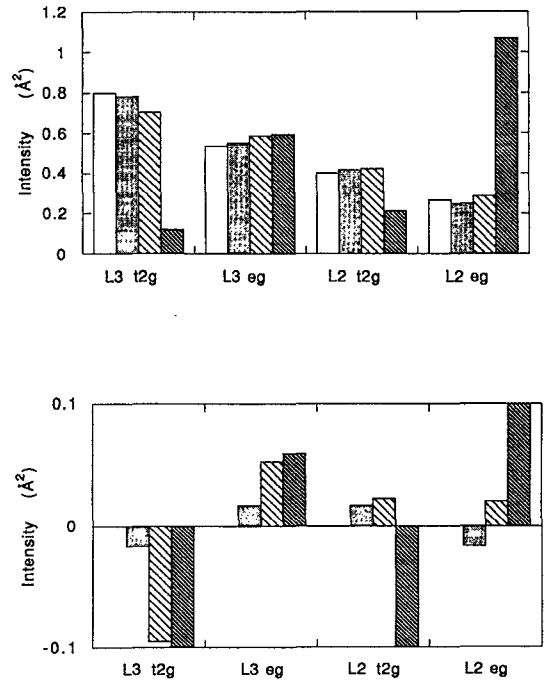

FIG. 2. The effects of $3d$ spin–orbit coupling and the pd multiplet effects on the single-particle result of Ti^{4+}. First column (blank): single-particle result. Second column (grey): inclusion of $3d$ spin–orbit. Third column (shaded): 10% of the pd multiplet effect. Fourth column (narrow shaded): the full atomic pd multiplet effect. The curves at the bottom indicate the differences with the single-particle result.

II. 3D SYSTEMS WITH AN EMPTY BAND

As an example of a $3d$ system we discuss tetravalent titanium, present in, e.g., $SrTiO_3$. The titanium ions are described as Ti^{4+} with a $3d^0$ ground state configuration. At the $L_{2,3}$ edge a $2p$ electron is excited to an empty $3d$ state and the final state configuration is described as $2p^5 3d^1$, i.e., the spectral shape relates to the distribution of empty $3d$ states in the presence of a $2p$ core hole.

A. The single-particle model

Neglecting all interactions the transition from $3d^0$ to $2p^5 3d^1$ is given by the energy difference between the two configurations. Within the calculations this is determined by a Hartree–Fock calculation which is not quantitatively adequate to reproduce the experimental energy differences exactly.[6] The theoretical excitation energy of Ti^{4+} is 465 eV. The intensity of the transition is given as the radial matrix element squared times the number of empty $3d$ states. The theoretical line spectrum is broadened with a Lorentzian of 0.3 eV related to the lifetime broadening. The spectrum is then convoluted with a Gaussian of 0.3 eV to simulate a typical experimental resolution. Figure 1 gives this spectrum in the top panel. Including the $2p$ spin–orbit coupling splits the edge into its L_3 and L_2 constituents with an intensity ratio of 2:1. The splitting is given as $\frac{3}{2}\cdot\zeta_{2p}$, which equals 5.65 eV. In the bottom panel an octahedral crystal field of 1.5 eV has been included. Its consequence is a splitting of the L_3 and L_2 edges into the t_{2g} and e_g symmetry peaks, split by 1.5 eV and with an intensity ratio related to the number of holes present in the t_{2g} and e_g bands, respectively, six and four. With $2p$ spin–orbit and crystal field a single-particle model gives four peaks with relative intensities: $L_3{:}t_{2g}; L_3{:}e_g; L_2{:}t_{2g}; L_2{:}e_g = 6,4,3,2$.

B. $3d$ spin–orbit coupling and multiplets

We now investigate the interactions which can cause a difference between the L_3 and L_2 edge. Important are the $3d$ spin–orbit coupling and $2p3d$ multiplet effects. At the top of Fig. 2 the integrated cross sections are given and at the bottom their differences with the single-particle result (blank column). The $3d$ spin–orbit coupling of the $2p^5 3d^1$ configuration of Ti^{4+} is 0.03 eV. Including it into the single-particle model slightly modifies the intensity ratios of the t_{2g} and e_g peaks of both the L_3 and L_2 edges. For the L_3 edge the t_{2g} peak decreases by -0.015 and the second peak increases by exactly the same amount. For the L_2 edge the effect is reversed. The $3d$ spin–orbit coupling does not transfer intensity from the L_2 edge to the L_3 edge.

The other interaction to be included are the $2p3d$ multiplet effects. They originate from the two-electron Coulomb $(\langle 2p3d|1/r_{1,2}|2p3d\rangle)$ and exchange $(\langle 2p3d|1/r_{1,2}|3d2p\rangle)$ integrals. To calculate these integrals they can be expanded in a series of Legendre polynomials.[6] For the pd Coulomb interaction this gives two terms denoted with the Slater integrals F^0 and F^2. The pd exchange interaction yields G^1 and G^3.[6] The F^0 term is the direct potential of the core hole and we have already included its energy into the average excitation energy. The combined effect of F^2, G^1,

TABLE I. The interaction strengths (in eV) as used in the calculations. Atomic values are used and the crystal field strength is adjusted empirically.

Ion	Ti^{4+}	Zr^{4+}	Mo^{6+}
Energy	464.8	2260.4	2572.8
$2p$ spin–orbit	3.77	57.26	71.24
Crystal field	1.5	3.0	4.0
d spin–orbit	0.03	0.09	0.16
F^2_{pd}	5.04	1.28	2.32
G^1_{pd}	3.70	1.04	1.93
G^3_{pd}	2.10	0.60	1.12

and G^3 is denoted as $2p3d$ multiplet effects. For Ti^{4+} the values of the Slater integrals are large. Table I collects the values of the parameters used for Ti^{4+}, Zr^{4+}, and Mo^{6+}.

For the third column in Fig. 2 the Slater integrals are normalized to 10% of their atomic values. The difference spectra of the 10% results show that the L_3 edge is more affected by the Slater integrals and the effects are larger than the $3d$ spin–orbit effects. For the L_2 edge the effect is smaller and both t_{2g} and e_g intensity increase, indicating that there is a considerable weight transfer from the L_3 to the L_2 edge. The effects of the atomic values of the pd Slater integrals (which are the actual values in ionic solids) are enormous and the relation to the single-particle scheme is completely lost. Another consequence is that one can reach seven possible final states,[3] three of which are "dipole forbidden" in a single-particle calculation. Table II collects the numerical results of the intensities of the L_3 and L_2 edge. Essentially one can state that the t_{2g} state of the L_3 edge is split in four, while all other peaks are not split. A detailed comparison with experiment has been discussed in Ref. 3.

III. 4D SYSTEMS WITH AN EMPTY BAND

The $4d$ transition metal compounds behave differently and the $2p4d$ multiplet effects do not play such an important role. For Zr^{4+} and Mo^{6+} the atomic value of F^2_{pd} is much smaller than the $2p$ spin–orbit coupling (Table I). Thus contrary to $3d$ systems, the multiplet effects are not able to change the L_3:L_2 ratio significantly. However, the pd multiplet effects are still of the same order of magnitude as the crystal field strength and they can be expected to modify the intensities of the t_{2g} and e_g peaks. The $4d$ spin–orbit coupling is larger than the $3d$ spin–orbit coupling, though still smaller than the pd Slater integrals and its effect on the intensity ratio is small.

TABLE II. Theoretical peak intensities in the $L_{2,3}$ spectra of Ti^{4+}. The total intensities of the "single-particle-like" peaks are indicated in boldface. All intensities in Å^2.

Edge	Subband band	Single particle	+3d spin–orbit	+pd multiplets (10%)	+pd multiplets (atomic)
L_3	t_{2g}	**0.800**	**0.783**	**0.705**	**0.119**
			0.383	0.005	0.009
			0.400	0.071	0.012
				0.612	0.025
				0.017	0.071
	e_g	**0.533**	**0.550**	**0.603**	**0.593**
L_2	t_{2g}	**0.400**	**0.416**	**0.422**	**0.213**
	e_g	**0.267**	**0.251**	**0.286**	**1.073**

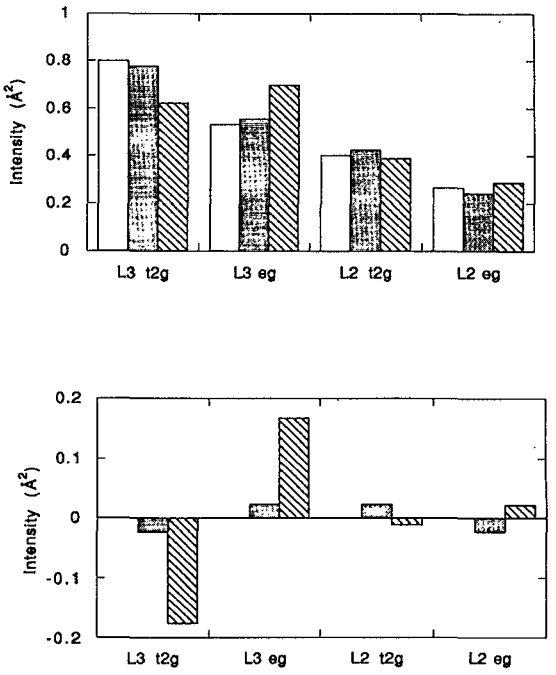

FIG. 3. The effects of $4d$ spin–orbit coupling and the pd multiplet effects on the single-particle result of Zr^{4+}. First column (blank): single-particle result. Second column (grey): inclusion of $4d$ spin–orbit. Third column (shaded): the atomic pd multiplet effect. The curves at the bottom indicate the differences with the single-particle result.

Figure 3 gives the integrated cross sections for Zr^{4+} at the top. At the bottom their differences with the single-particle result (blank column) are given. The first column (grey) shows the effect of the $4d$ spin–orbit coupling, and for the second column (shaded) the $2p4d$ Slater integrals have also been added. The effect of the Slater integrals is larger. They are more important for the L_3 edge, related to the fact that in analogy to titanium only the L_3 edge is split into more states. Thus in contrast to $3d$ systems where pd multiplet effects completely dominate the spectral shapes, we find for the $4d$ systems that the pd multiplet effects are too small to affect the intensity ratio of the L_3 and L_2 edge which is always close to 2:1. However, the edges are not identical because the pd multiplet effects, and to a minor extent the $4d$ spin–orbit coupling, cause a weight transfer from the t_{2g} to the e_g peaks.

An important consequence of the present analysis is that for $4d$ systems the L_3 edge is more affected by the multiplet effects than the L_2 edge. Hence if one would like to interpret the x-ray absorption results with a single-particle model, the L_2 edge is better suited. As can be seen in Fig. 3, the effects due to both $4d$ spin–orbit interaction and multiplet effects are of the order of 5% to 7% for the L_2 edge, while they are of the order of 20% to 30% for the L_3 edge. A similar rea-

soning has been used for $3d$ systems by Borg and co-workers.[15] However, as discussed above, for $3d$ systems the multiplet effects are large, which modifies the spectral shape to such an extent (such as the splitting between t_{2g} and e_g peaks) that the analysis with single-particle interpretations also loses its quantitative significance for the L_2 edge.

The present calculations are limited to a d final state that does not possess any energy spread apart from a splitting in a cubic crystal field. Effects from symmetry distortions and from energy dispersion of the valence band (in presence of the core hole) as determined from *ab initio* single-particle calculations are not included.

IV. 4D SYSTEMS WITH A PARTLY FILLED BAND

Systems with a partly filled d band are subject to strong intraband $4d$–$4d$ correlation effects. For the d^n initial states, the dd multiplet effects result in a number of states spread over some eV. They are known as Tanabe–Sugano diagrams and used as such in optical spectroscopy.[16] In solid state theory the dd multiplet effects are "reformulated" as the Stoner exchange splitting and orbital polarization effects. In Ref. 17 the formulas are given to transfer the values of the dd Slater integrals to J and C values, which are related, respectively, to the spin- and orbital-polarization effects. For a review paper see Ref. 18.

For the $L_{2,3}$ edges the most important effect of the dd multiplets is that they determine the symmetry of the ground state (according to Hund's rules). For $3d$ transition metal compounds with a partly filled $3d$ band detailed multiplet calculations have been published.[4] We focus here on the $4d$ systems for which little is known about the interplay between pd and dd multiplet effects. Figure 4 shows the results of multiplet calculations for the L_3 (solid) and L_2 (dashed) spectra of molybdenum for valencies from 6+ ($4d^0$; bottom) to 0+ ($4d^6$; top). The spectra have been aligned and normalized to the peak height of the L_3 edge. The L_2 edge is shifted over the $2p$ spin–orbit splitting and multiplied by 2. The spectra have been calculated using a reduction of 50% for the dd Slater integrals and a reduction of 75% for the pd Slater integrals. This reduction is used to simulate the fact that the ground state is not pure $4d^n$ but has an admixture of $4d^{n+1}\mathbf{L}$, where $\mathbf{L}$ denotes a hole in the valence band of the ligand. These charge transfer effects can in principle be included by carrying out charge transfer multiplet calculations,[19] but this is out of the scope of the present analysis. A crystal field splitting of 4.0 eV has been used and as a result all $4d^n$ states are in a low-spin ground state. Thus in going through the series from the bottom ($4d^0$) to the top ($4d^6$) one fills in every step one t_{2g} hole. Because the number of t_{2g} holes decreases from six to zero while the number of e_g holes is four in all cases, in a single-particle interpretation the intensity of the first peak will decrease linearly with the number of holes. The multiplet effects (and the $4p$ spin–orbit coupling) modify this picture slightly in a similar fashion as for the systems with an empty $4d$ band. One can observe that both for the L_3 and the L_2 edge the intensity of the t_{2g} peak indeed decreases. One notices that this effect is stronger for the L_2 edge which for the $4d^4$ system becomes very small. In connection with this the intensity ratio, which is 2:1 for $4d^0$,

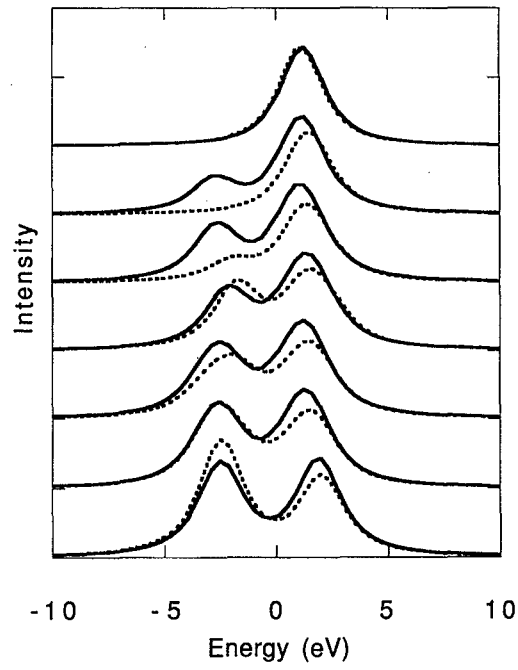

FIG. 4. Crystal field multiplet calculations for molybdenum. The L_3 edge (solid line) and the L_2 edge (dashed) are given for Mo^{6+}, $4d^0$ (bottom) to Mo^{0+}, $4d^6$ (top). From bottom to top every time one $4d$ electron is added. The spectra have been aligned and normalized to their peak height.

is changing as a consequence of the rapidly decreasing t_{2g} peak of the L_2 edge. For a $4d^5$ ground state the t_{2g} peak even disappears completely for the L_2 edge, while it remains clearly present for the L_3 edge. Finally, for the $4d^6$ systems the L_3:L_2 ratio is again 2:1 and there is only one peak present, since there are no t_{2g} holes left.

The main reason for the observed behavior are the effects of dd multiplet effects and $4d$ spin–orbit coupling on the initial state. We can illustrate this for the "missing" t_{2g} peak of $4d^5$. The ground state of the low-spin $4d^5$ state in octahedral symmetry is $^2T_2$. If one excites a $2p$ electron to the single t_{2g} hole the final state has the configuration $2p^5t_{2g}^6$, which has the symmetry $^2T_1$. Including the $2p$ spin–orbit coupling one splits the $^2T_1$ state into an E_1 (related to the L_2 edge) and a G (related to the L_3 edge) state.[16] If one includes also the $4d$ spin–orbit coupling, the $^2T_2$ ground state is split and the new ground state is the E_2 state, while the G state is shifted by an energy related to the $4d$ spin–orbit coupling. A dipole transition is possible from the $4d^5[E_2]$ ground state to the $2p^64d^6[G]$ final state but not to a final state with E_1 symmetry. Hence the t_{2g} hole cannot be reached at the L_2 edge. Without the $4d$ spin–orbit coupling both the E_2 and G initial states are degenerate and a dipole transition is possible for both the L_3 and the L_2 edge. The calculation with and without $4d$ spin–orbit coupling is indicated in Fig. 8 (see Sec. V). This absence of a second peak at the L_2 edge has been observed by Sham[14] who used a similar argumentation. The stronger decrease of the intensity of the t_{2g} peak in the L_2 edge in Fig. 4 has a similar origin. Due to dd Slater integrals (the ground state symmetry) and $4d$

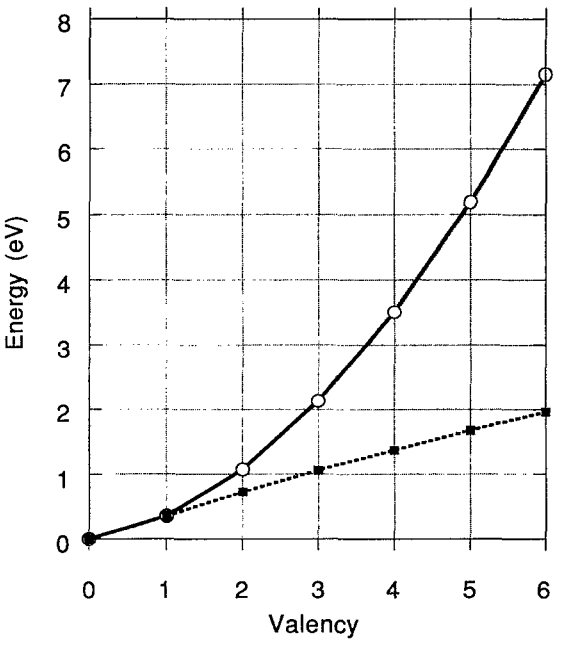

FIG. 5. The calculated energy shifts for molybdenum. Indicated are the energy differences with Mo^{0+} (solid line, circles) and the energy differences of Mo^{n+} with the system with one valency lower (dashed, squares). For the plot the calculated HF results are divided by 2.

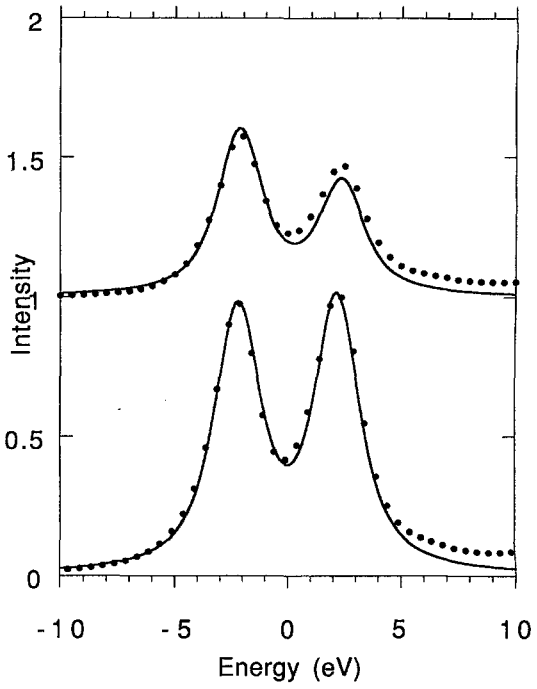

FIG. 6. Comparison of a crystal field multiplet calculation of Mo^{6+}, $4d^0$ (solid line) with an experimental spectrum of gas-phase MoF_6 (points). Both the L_2 edge (top) and the L_3 edge (bottom) have been aligned at zero.

spin–orbit coupling some transitions are forbidden at the L_2 edge. This is also the reason for the observed changes in the intensity ratio of the L_3 and the L_2 edge.

We would like to discuss the shifts between the spectra of compounds with different valencies. In the calculations the average energy positions of the $4d^n$ initial states and the $2p^5 4d^{n+1}$ final states are determined. It has been found for the $3d$ systems that the calculated shifts are too large by about a factor of 2.[20] Figure 5 shows the relative energy positions of the different valencies. The calculated energy differences have been reduced by a factor of 2. The solid line gives the energy difference with respect to Mo^{0+} and the dashed line compares a given valency with the system with one valency lower. We find theoretically that the energy shift is about 1 to 2 eV per unit valency change and the shifts increase for higher valencies. It is noted that at higher valencies the systems become more covalent, which will counteract the calculated ionic shifts.

V. COMPARISON WITH EXPERIMENTS

We compare the results of our crystal field multiplet calculations with x-ray absorption experiments for MoF_6 molecules and the solids $CsNbF_6$ and $Ru(NH_3)_6Cl_6$. Details on the materials and the experiments can be found in Refs. 21 and 22.

Figure 6 compares the experimental spectrum of MoF_6 with a crystal field multiplet calculation. The calculation has been performed for Mo^{6+}, $4d^0$. The Slater integrals (Table I) have been reduced to 75% of their atomic values to account for charge transfer effects.[18] A cubic crystal field of 4.5 eV was fitted to the experiment. For large values of the crystal field, the observed splitting directly represents the crystal field splitting, which is not so for small crystal field splittings.[3] The theoretical line spectrum was broadened with a lifetime broadening (2Γ=2.0 eV). The spectrum was then convoluted with a Gaussian (σ=0.4 eV) to simulate the experimental broadening. The L_3 and L_2 spectra have been aligned with respect to the calculated ones. In this paper we concentrate on the differences between the L_3 and L_2 spectra and it can be observed that these differences are nicely reproduced. This indicates that the pd multiplets, and to a minor extent the $4d$ spin–orbit coupling, correctly describe the differences between the L_3 and L_2 spectra.

Figure 7 compares the experimental spectrum of solid $CsNbF_6$ with the result of a crystal field multiplet calculation. The procedure followed is similar as for Fig. 6. The calculation has been performed for Nb^{5+}, $4d^0$, with Slater integrals reduced to about 40% of their atomic values, a crystal field of 3.4 eV, and broadenings with a Lorentzian of (2Γ=2.0 eV) and a Gaussian of 0.7 eV. Again the differences between the L_3 and L_2 spectra are nicely reproduced.

Comparing the simulations for solid $CsNbF_6$ with those for the MoF_6 molecule, there is a noticeable difference in the magnitude of the Slater integrals. For the solid the Slater integrals are reduced more (by 40% vs 75%). The Slater integral reduction is related to the covalency, hence solid $CsNbF_6$ is found more covalent than the MoF_6 molecule. For trivalent $3d$ transition metal fluorides it was found that atomic Slater integrals could be used.[3] The origin of this difference is partly due to the higher covalent nature of $4d$ systems and partly the high valency of niobium (5+) and

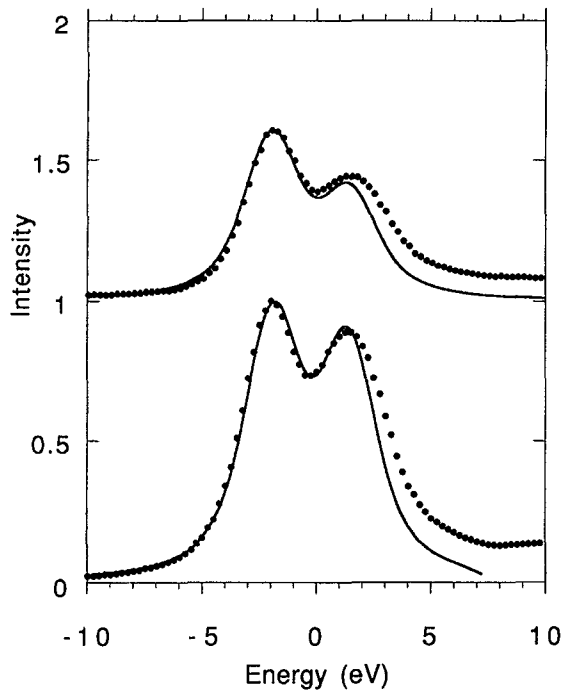

FIG. 7. Comparison of a crystal field multiplet calculation of Nb^{5+}, $4d^0$ (solid line) with an experimental spectrum of solid state $CsNbF_6$ (points). Both the L_2 edge (top) and the L_3 edge (bottom) have been aligned at zero.

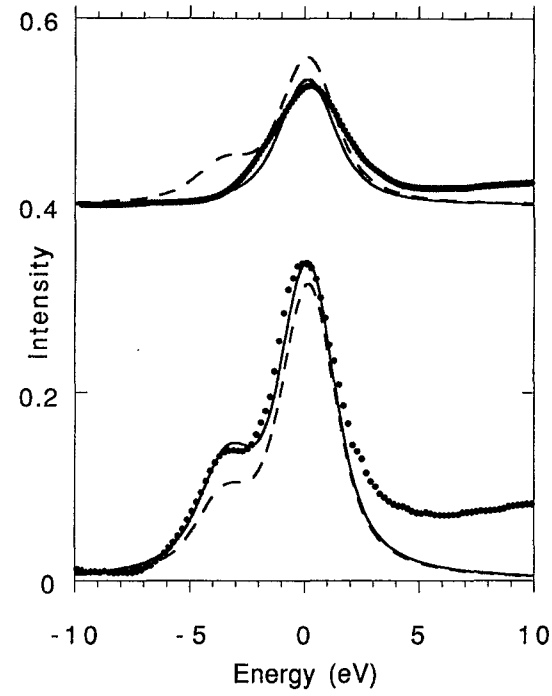

FIG. 8. Comparison of a crystal field multiplet calculation of Ru^{3+}, $4d^5$ (solid line) with an experimental spectrum of solid state $Ru(NH_3)_6Cl_6$ (points). Both the L_2 edge (top) and the L_3 edge (bottom) have been aligned at zero. The corresponding spectra with the $4d$ spin–orbit coupling set to zero are indicated with the dashed lines.

molybdenum (6+). Simulations for $KMnO_4$ (manganese 7+) and K_2CrO_4 (chromium 6+) also reveal that the Slater integrals must be reduced to values of the order of 30% of the atomic values.[23,24] By comparing Fig. 6 with Fig. 7, one observes that reducing the Slater integrals increases the intensity of the t_{2g} peak. In the extreme case that the Slater integrals are reduced to zero one arrives at the single-particle result.

Figure 8 compares the experimental result for solid $Ru(NH_3)_6Cl_6$ with the result of a crystal field multiplet calculation. The calculation has been performed for Ru^{3+}, $4d^5$, with Slater integrals reduced to about 25% of their atomic values, a crystal field of 3.65 eV and broadening by a Lorentzian of ($2\Gamma=2.0$ eV) and a Gaussian of 0.7 eV. As discussed above the differences between the L_3 and L_2 spectra are special in this case because in the spectrum of the L_2 edge the t_{2g} peak is absent. The dashed line gives the result if one puts the $4d$ spin–orbit coupling to zero; as discussed above the t_{2g} peak of the L_2 edge is then present. Note the large reductions in the values of the Slater integrals, now for a system with a relatively low valency, but with more covalent ligands. This strong reduction indicates that for $4d$ systems the Slater integrals are reduced more than for the equivalent $3d$ systems. Apart from this the atomic values themselves are also smaller for $4d$ systems (see Table I).

For a more complete study, including a comparison with similar observations in optical spectroscopy, it is necessary to simulate a large series of compounds within the same model. This can yield a database similar to that obtained from optical spectroscopy, determining both the crystal field parameters and the Slater integral (or Racah) parameters indicating the "degree of covalency." Because of the site and element selectivity of x-ray absorption, systems with a number of transition metal ions present, and/or with low concentrations of different transition metals, can be measured more easily.

A problem arising is that the crystal field multiplet model is less applicable to strongly covalent systems (also if applied to optical spectroscopy). One has to use the configuration interaction (charge transfer) model to obtain more reliable results.[18] Within the charge transfer multiplet model the effective crystal field parameters and the effective Slater integral parameters are different then those obtained from the crystal field multiplet model. Additionally one obtains the contributions of the individual configurations participating in the Hamiltonian (e.g., $4d^n$ and $4d^{n+1}\mathbf{L}$). Within the charge transfer model the "degree of covalency" is defined as the contribution from the $4d^{n+1}\mathbf{L}$ configuration. It can be shown that there is a close relation with the Slater integral reduction within the crystal field multiplet model. For a detailed discussion see Ref. 18 and references therein.

VI. CONCLUDING REMARKS

The differences between the L_3 and L_2 edges have been shown to be caused mainly by pd multiplet effects. The pd multiplet effects are considerably larger than the $3d$ or $4d$ spin–orbit coupling which lead to small additional effects.

For $3d$ systems one finds that the pd multiplets also dominate the $2p$ spin–orbit coupling. As a consequence the $L_{2,3}$ spectrum does not correspond to the spectrum expected

in a single-particle picture; instead detailed multiplet calculations are necessary to reveal the spectral shape, both for systems with empty and partly filled $3d$ bands.

For $4d$ systems, the $2p$ spin–orbit coupling is large and the L_3 and L_2 spectra have an intensity ratio close to 2:1. The differences between the L_3 and L_2 edge originate from the intensity transfer between the t_{2g} and e_g peaks due to pd multiplet effect and to a minor extent due to $4d$ spin–orbit coupling. The L_2 edge is affected less by multiplet effects than the L_3 edge, which makes it preferable to use L_2 spectra when comparing with the results of single-particle calculations. For systems with a partly filled $4d$ band, the 2:1 ratio of the L_3 and L_2 edge is affected by a combination of the ground state symmetry (dd multiplet and crystal field effects) with $4d$ spin–orbit coupling.

Comparison with experiment shows that the experimental spectra can be simulated accurately. The Slater integrals must be reduced from their atomic values indicating strong covalency. Covalency is found to be stronger for the equivalent $4d$ systems as compared to $3d$ systems.

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